Indian J Phys **51B**, 8-16 (1977)

Microwave spectrum and barrier to internal rotation in N-methyl pyrazole

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The microwave spectrum of N-methyl pyrazole was measured in the range 18-32 GHz. Transitions of A- and E-species were assigned and the spectroscopic constants and the height of barrier opposing internal rotation was derived by an IAM procedure applicable to low barriers. This treatment gave $I_\alpha = 3.155$ amu Å^2 for the moment of inertia of the methyl group and $V_3 = 530$ cal mol^{-1} for the barrier to internal rotation.

1. INTRODUCTION

Barriers to internal rotation for methyl groups attached to planar rings with aromatic character have been studied in about twenty substances by microwave spectroscopy. The three-fold barrier term V_3, in such cases becomes zero for reasons of symmetry when the aromaticity gives the ring a C_{2v} axis coincident with the ring methyl bond. When the symmetry is destroyed by substitution, three-fold barrer contributions appear which reflect the asymmetry of the ring with respect to the ring-methyl axis. Such effects are well illustrated for substituted benzene[1] and pyridines[2]. In methyl derivatives of planar five-membered heterocyclic rings, V_3 is zero for the above reasons. N-methyl pyrrole[2] and its symmetric derivatives are the examples. Nearly a dozen or so cases have been studied[2,3] for other methyl positions of the ring. From these investigations it was found that, although the symmetries of such rings are less than those of benzene-like structures, the V_3 terms are commonly less than 1 Kcal mol^{-1} and that[4] the lower V_3 values are associated with higher aromaticity in the parent rings as indicated, for example, by bond distances of Zeeman effects[2].

Methyl barriers for 3- and 5-methyl pyrazoles were determined to be 429 and 333.0 cal mol^{-1} respectively by Srivastava and Sheridan[5]. In relation to these studies, it seemed very interesting to study the microwave spectra of N-methyl pyrazole. On account of high aromaticity of such rings, it is expected to give a low value of the barrier.

2. Experimental

The sample of N-methyl pyrazole was procured commercially. The liquid was twice vacuum distilled and was used without further purification. Measurements were made at room temperature (nearly 22°C) and the pressure in the stark cell was varied from 10 to 15 m.Torr. The rotational absorption spectrum was observed in the frequency range from 18.0 GHz to 32.0 GHz with a conventional stark modulation spectrograph, and a fast scan in the region 34.5 to 38.5 GHz was recorded on Hewlett Packard spectrometer at University College of London.

3 Prediction of Spectra from Assumed Geometry

Nygaard et al[6] and Pozdeev et al[7] have determined the structure of pyrazole. The structure of pyrazole ring was taken as that obtained by Nygaard et al[6]. It was further assumed that the substitution of CH_3 group does not change the structure of pyrazole. The bond lengths and bond angles have been tabulated in table 1. With this assumed structure and methyl group with reasonable CH_3 and CC parameters added, the rigid rotor rotational constants A, B and C are predicted as follows :

A — 8941.6 MHz; B = 3737.3 MHz, C = 2679.4 MHz

Although such predictions are of limited value for spectra expected to show large vibration rotation interactions, the differences in the rotational constants

Table 1. Assumed structure of N-methyl pyrazole

Bond lengths (A)			Bond angles (Degree)		
$N_1 - N_2$	=	1.349	$\angle CN_1N_2$		118.4
$N_2 - C_3$	=	1.331	$\angle N_1N_2C_3$	=	104.1
$C_3 - H$	=	1.078	$\angle N_2C_3H$	=	119.3
$C_3 - C_4$	=	1.416	$\angle HC_3C_4$	=	128.8
$C_4 - H$	=	1.076	$\angle C_3H_4H$	=	127.9
$C_4 - C_5$	=	1.372	$\angle HC_4C_5$	=	127.6
$C_5 - H$	=	1.077	$\angle C_4C_5H$	=	132.1
$C_5 - N_1$	=	1.359	$\angle HC_5N_1$	=	121.5
$N_1 - C$	=	1.450	$\angle C_5N_1C$	=	128.5
$(C-H)_{methyl}$	=	1.091	$\angle N_1CH$	=	111.2

Table 2. Rotational constants of N-methyl pyrazole from the assumed geometry

A	8941.585	MHz
B	3737.314	MHz
C	2672.399	MHz
k	−0.662126	
I_a	56.520	amu Å^2
I_b	135.225	amu Å^2
I_c	188.616	amu Å^2
$I_a + I_b$	3.129	amu Å^2

Table 3. Experimental values of rotational and centrifugal distortional constants obtained by least square fitting from the A-state spectrum

A	8970.107	±	0.104	MHz
B	3745.544	±	0.092	MHz
C	2682.667	±	0.086	MHz
D_J	0.00108	±	0.00017	MHz
D_{JK}	−0.00476	±	0.0015	MHz
D_K	−0.03094	±	0.0144	MHz
DD_J	0.0 assumed			MHz
DD_K	−0.00135	±	0.0009	MHz
I_a	56.340			amu Å^2
I_b	134.927			amu Å^2
I_c	188.386			amu Å^2
$I_a + I_b + I_c$	2.881			amu Å^2

Using the conversion factor of 505376 MHz per amu Å^2

Table 4. Internal rotor constants of the methyl top in N-methyl pyrazole

V_3	530.1	±	0.7	cal mol^{-1}
I	3.155	±	0.004	amu A^2
λ_z	0.99962			assumed

were well predicted and gave useful guidance in the assignment of simultaneously observed spectra.

The dipolar properties of the methyl pyrazole could be predicted from the known dipole[6] of pyrazole (2.21D) directed along a line almost parallel to the C(5)-H bond and virtually perpendicular to the N(2)—C(3) bond. The predicted values of dipole moment components of N-methyl pyrazole is as follows :

$\mu_a = 0.67$ D, $\mu_b = 2.12$ D, μ_c 0.

Thus the molecule is expected to show strong b-type transitions and the a-type ransitions are relatively weak.

With these values of A, B, C obtained from the assumed geometry and these values of μ_a, μ_b and μ_c the frequencies of the spectral lines together with their relative intensities were calculated using a computer programme, in the frequency region from 12 to 40 GHz for J from 0 to 20. The region of interest was sorted out and the spectrum was recorded on the conventional 100 KHz stark modulation spectrograph in the frequency region from 18.0 to 32.0 GHz at room temperature

4. Treatment of Internal Rotation

The theory of Internal Axis Method (IAM) for calculating the internal rotor splittings is due to Hecht and Dennison[8] with the high barrier approximation omitted by Tipton, Coffey and Boggs[9] The physical model chosen for the formulation of the internal rotation problem consists of a rigid symmetric top (CH_3 group) attached to a rigid frame, which may or may not be symmetric. The symmetric top (CH_3) is regarded as rotating with respect to the other part which is taken as the frame work. The input parameters of the computer program are : A, B and C, the V_3 barrier height or the reduced potential s, λ_z and I_α which are inter-related by :

$$V_3 = (9/4)\ F\ s$$

$$F = \hbar^2/2r\ I_\alpha,$$

$$r = 1 - \lambda_x \rho_x - \lambda_z \rho_z,$$

$$\rho_g = \lambda_g\ I_\alpha / I_g$$

The subscript g stands for x, y, z axes in the molecule, λ_g are the direction cosines of the top axis with respect to the principal axes and I_α is the moment of inertia of the top about its symmetry axis. Approximate Mathieu eigen values are also given for the v and v+1 torsional state. We have

5. Assignment and Analysis of Spectra

From the stark effect some of the lines belonging to R- and Q-branch series could be labelled but the identification of J values could not be done due to the crowded spectrum.

The splittings of the spectral lines for the A and E states were calculated by Internal axis method (IAM) using a computer program of Tipton, Coffey and Boggs[9]. Srivastava and Sheridan[5] obtained the value of barrier height for 3- and 5-methyl pyrazoles to be 429 and 333 cal mol^{-1} respectively. It was, therefore, guessed that the value of barrier height for this melecule should also be somewhere between 300 and 600 cal mol^{-1}. The (A/E) splittings were calculated for such barrier heights assuming a value of $I_c = 3.135$ Å^2. From the calculations of (A/E) splittings those Q-branch transitions showing close doublets were picked up and a graph between (A/E) splitting vs barrier height was plotted. These Q-branch doublets were searched in the recorded spectrum and the Q-branch A-state lines were picked up for tentative assignment of the spectra and a rough estimate of the barrier height was made with the observed splittings from the (A/E) splitting vs barrier height curve. The doublet at 26004.00 MHz and 26018.75 MHz frequencies with a separation of 14.75 MHz was recorded. No other doublet having similar nature and stark effect was recorded in this region. This doublet was suspected to be $11_{29} - 11_{38}$ transition. -14.75 MHz splitting corresponds to a barrier to 530 cal/mole and +14.75 MHz to a barrier of more than 600 cal/mole. The doublet at 21812.60 MHz and 21835.60 MHz were recorded with a separation of 23 MHz which was suspected to be $9_{27} - 9_{36}$ transition. The splitting of −23 MHz corresponds to a barrier of 541 cal mol^{-1} and +23 MHz corresponds to a barrier of 598 cal mol^{-1}. Another doublet appearing at 26487.4 MHz and 26509.95 MHz was recorded with a separation of nearly 22 MHz which was suspected to be of $9_{18} - 9_{27}$ transition. +22 MHz splitting corresponds to a barrier height of more than 600 cal mol^{-1} and a splitting of −22 MHz corresponds to a barrier of 538 cal mol^{-1}. More consistent value of barrier height corresponds to the negative values of splittings for the above transitions viz. $11_{29} - 11_{38}$, $9_{27} - 9_{36}$ and $9_{18} - 9_{27}$. It was guessed that the value of V_3 should lie between 500 and 550 cal mol^{-1}. Thus it was suggested that the A line of $11_{29} - 11_{38}$, $9_{27} - 9_{36}$ and $9_{18} - 9_{27}$ are respectively at 26004.00 MHz, 21812.6 MHz and 26487.4 MHz.

A graph between $\frac{\nu_{obs}}{\Delta E(k)} = \frac{A-C}{2}$ vs k was plotted, for the tentatively assigned A-species of the transitions $11_{29} - 11_{38}$, $9_{27} - 9_{36}$ and $9_{18} - 9_{27}$ which gave a value of $\frac{A-C}{2} = 3144.0$ and $k = -0.6619$. With these values of k

and $\frac{A-C}{}$ low J transitions were predicted and assigned. The low J transitions used for the plot are :

3_{21}-3_{38}, 5_{23}–5_{32}, 5_{15}-5_{24}, 6_{24} 6_{33}, 6_{25}-6_{34} and 6_{16}–6_{25}.

Other Q-branch lines were predicted and assigned with the known values of k and $(-\frac{A-C}{2})$ determined from the graph of low J lines given in table 5.

Table 5. Observed and calculated frequencies in MHz of N-methyl pyrazole in its ground state

Transition	A		E	A/E Splitting	
	Obs	Obs -Calc.	Obs.	Obs.	Obs -Calc.
R-branch					
1_{11} – 2_{20}	30803.10	0 43	31898 43	-1095 33	-1 67
1_{10} – 2_{29}	29593.07	-0.45	28173.00	+1420 07	-0 43
2_{20} – 3_{39}	21912.80	+4 46	--		--
3_{03} – 4_{14}	26523 90	-0.13	26444 30	79.60	0 40
4_{04} – 5_{15}	31095.00	0 32	31033 00	62 00	-0 15
4_{11} – 5_{05}	27663 00	-0 78	27713 30	-50 25	-0 65
5_{24} – 6_{15}	30170 00	0 26	30543 00	-371 50	-2.50
Q-branch					
3_{21} – 3_{30}	28166 90	0 16	28729 00	-563 50	-1 40
5_{32} – 5_{32}	25923.50	0 58	26855 30	-931 80	-3 80
5_{15} – 5_{24}	25667 50	0 05	25305 50	362 00	2 00
6_{16} – 6_{25}	29074.50	0 46	28814 50	260 00	0 90
6_{06} – 6_{15}	22050 40	-0 07	22043 70	16 70	-0 09
6_{24} – 6_{33}	24260 70	0 40	25010 25	-749 54	-0.54
6_{25} – 6_{34}	31098 00	-0 50	29813 29	1284.72	-1 28
7_{07} – 7_{16}	27823.00	0 24	27789 40	33.60	-0 01
9_{27} – 9_{36}	21812.60	-0.57	21835 60	-23 00	-1.00
9_{18} – 9_{27}	26487.40	0 46	26509.95	-22.55	-0 80
10_{28} –10_{37}	23173.80	0.63	23170.00	3.80	-0 70
11_{38} –11_{47}	29769 69	-0.37	30022 80	-253 11	-0.11
11_{29} –11_{38}	26004.00	-0.56	26018 75	-14.75	-1 05
12_{39} –12_{48}	28561.00	0 51	28709.37	-48.37	-1 87
$14_{3,11}$–$14_{4,10}$	30592.11	-0.09	30592.11	0.00	-0.30

The A-state spectrum for the ground torsional state has been calculated for different values of the barrier height V_3 using IAM programme written by Tipton et al.[9] In order to get the theoretical pseudo rotational constants at different values of the barrier height, the least squares fit of the calculated frequencies of the A-state spectrum on the rigid rotor model was carried out. The above curve was plotted for 3-Me Pyrazole[5] from which the predicted value of barrier height corresponding to observed $I_a+I_b-I_c$ was found to be 415 cal mol^{-1} which agrees reasonably well with the experimentally determined value of 429 cal mol^{-1}. The predicted value of barrier height from the same curve for 5-Me Pyrazole[5] was found to be 300 can mol^{-1} corresponding to observed $I_a+I_b-I_c$, which also agrees well with the experimentally determined value of 333 cal mol^{-1}. It was therefore, expected to predict reasonably well the barrier of N-methyl pyrazole for a given value $I_a+I_b-I_c$. The barrier was guessed to lie within 500 and 550 cal mol^{-1} from the Q-branch doublets. From the curve the corresponding values of $(I_a+I_b-I_c)$ comes out to be 2.88 amu Å^2 and 2.94 amu Å^2 respectively. With these values of $(I_a+I_b-I_c)$, (A+C) was predicted and the respective ranges of the R-branch lines were obtained. R-branch lines were picked up on the basis of (A/E) splittings and stark effect. The assigned R-branch lines are given in the table 5, along with (A/E) splittings.

A computer program, prepared by A. B Beauder was used with some modifications to get the best fit values of the rotational constans A, B, C and the centrifugal distortion constants D_J , D_{JK} , D_K, DD_J , and DD_K using fifteen Q-branch and seven R-branch lines in the least squares fit. The values of rotational and centrifugal distortion constants and $I_a+I_b-I_c$ are given in table 3. Though the assignments have been made, higher J transitions have not been taken into account in the least squares fit because of poor measurement of frequencies in the frequency region 34.5 GHz to 38.5 GHz. The uncertainty in frequency measurement in this region may be more than ± 2 MHz.

The values of $I_a+I_b-I_c$ = 2.882 amu Å^2 obtained from the least squares fit is considerably less than the value of 3.135 amu Å^2 for the case of two out-of-plane methyl hydrogens on a rigid rotor basis. This would be expected for a low barrier to methyl torsion, and these constants are accordingly to be regarded as pseudo rotational constants only.

A correction of 40 MHz was made for the rotational constant A, which corresponds to $I_a+I_b-I_c$ = 3.135. With these new values of rotational constants

A = 8930 00±1.0 MHz; B = 3745.54±0.1 MHz; C = 2682.67±0.1 MHz the (A/E) splitting for V_3 = 520, 530 and 540 cal mol^{-1} at I_{α} = 3.135, 3.157 and 3.185 amu Å^2 was calculated on the IAM program. These

calculated splittings were helpful in the assignment of E-species of the spectral lines. The spectral line obtained at 22060.4 MHz was assigned as the A-species of 6_{06}–6_{15} transition. Another line of the same intensity and stark pattern was recorded at 22043.7 MHz, which was assigned as the E-species of the 6_{06}—6_{15} transition. The (A/E) splitting of the line is+16.7 MHz which corresponds to the barrier height (V_3) = 530 cal mol^{-1} for I_χ = 3.150 and V_3 = 520 cal mol^{-1} for I_χ = 3.173 The A-species of the $14_{3,11}$–$14_{4,10}$ transition was observed at 30592.11 MHz and no other line was recorded in the near vicinity which means it is unsplit line, hence the transition $14_{3,11}$-$14_{4,10}$ gives the value of V_3 = 530 cal mol^{-1} and I_χ = 3.158 amu Å^2 from the plot of (A/E) splitting vs I_χ and V_3 = 530 cal mol^{-1}. For V_3 = 530 cal mol^{-1}, the E-partner of the A-transition 11_{29}-11_{38} at 26004.00 MHz should lie near 26019 MHz. A line of the same intensity as the A-transition, with a similar stark effect, was observed at 26018.75 MHz, which in turn indicated a V_3 of 532.7 cal mol^{-1} Other E-species lines were predicted and identified and are listed in Table 5. The values of V_3 and I_χ were determined by interation process from the graph. The average value of I_χ for V_3 = 530 cal mol^{-1} was determined to be 3.155 amuA^2. Keeping this value of I_χ constant, the average value of V_3 was determined to be 530.0 cal mol^{-1}.

6. Discussion

In several cases the differences between the observed and the calculated frequencies remained much larger which could not be included in the least squares fit procedure. The difficulty of better fitting arises due to following reasons :

(i) the non-rigidity effect and the missing V_6 term in the IAM calculation may not be negligible for such a low value of the barrier height V_3,

(ii) the effects of nuclear quadrupole hyperfine structure due to two nitrogen atoms may not be negligible.

For the present study these effects have not been taken into consideration, and

(iii) centrifugal distortion corrections have been taken into account incompletely.

Acknowledgments

We are thankful to Professor J. Sheridan for many helpful discussion and help and to Prof. D. J. Millen for providing the facilities to record the spectrum in the region 34.5 to 38.5 GHz. One of us (NKN) is thankful to the department of Atomic Energy Commission, for the financial assistance in the form of Senior Research Fellowship.

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